

## *Electronic Supplementary Information*

### **Synthesis of layered tantalate nanocrystals by aqueous process at room temperature**

*Takayuki Ban\*, Shogo Yoshikawa, Yutaka Ohya*

Department of Materials Science and Technology, Gifu University, Yanagido 1-1, Gifu 501-1193, JAPAN

Corresponding author [\*]

Takayuki Ban

Department of Materials Science and Technology, Gifu University, Yanagido 1-1, Gifu 501-1193, JAPAN

e-mail: ban@gifu-u.ac.jp    tel: +81 58 293 2585    fax: +81 58 293 2794

#### *(1) Synthesis procedure of $M_4Ta_6O_{17} \cdot nH_2O$ compounds*

For hexatantalates, three types of compounds were synthesized;  $Rb_4Ta_6O_{17} \cdot nH_2O$ ,  $H_4Ta_6O_{17} \cdot nH_2O$ , and  $(TMA,H)_4Ta_6O_{17} \cdot nH_2O$ .  $Rb_4Ta_6O_{17} \cdot nH_2O$  was synthesized by a solid state reaction, as follows:  $Rb_2CO_3$  powder (2.40 mmol) and  $Ta_2O_5$  powder (3.27 mmol) were mixed at a molar ratio of  $Rb/Ta = 4.4/6$ . The mixture was annealed at 800 °C for 2 h, and then ground by agate mortar and pestle. Further annealing at 1200 °C for 20 h and the subsequent heating at 150°C overnight resulted in the formation of  $Rb_4Ta_6O_{17} \cdot 2H_2O$ .

$H_4Ta_6O_{17} \cdot nH_2O$  was prepared from  $Rb_4Ta_6O_{17} \cdot 2H_2O$  by ion exchange. The synthesized  $Rb_4Ta_6O_{17} \cdot 2H_2O$  (0.4 g) was added to 2 M  $HNO_3$  aqueous solution (230 mL). This mixing ratio corresponds to  $H^+/Rb^+ = 500$ . The resulting suspension was stirred at 100 °C for 3 days. The powder was collected by centrifugation, washed with a copious amount of distilled water, and then allowed to dry under the ambient condition. Since the annealing of the obtained powder at 800 °C for 1 h provided  $Ta_2O_5$  powder, most  $Rb^+$  ions in the interlayers were likely ion-exchanged for  $H^+$ . Thus,  $H_4Ta_6O_{17} \cdot nH_2O$  was prepared.

$(TMA,H)_4Ta_6O_{17} \cdot nH_2O$  was prepared from  $H_4Ta_6O_{17} \cdot nH_2O$  by ion exchange. The synthesized  $H_4Ta_6O_{17} \cdot nH_2O$  (50 mg) was added to 0.12 M TMAOH aqueous solution (25 mL). This mixing ratio corresponds to  $TMA^+/H^+ = 20$ . The resulting suspension was stirred at 100 °C for 5 days. The powder was collected by centrifugation, washed with a copious amount of distilled water, and then allowed to dry under the ambient condition. This ion exchange shifted the peaks in the XRD patterns to lower angles. The XRD of the obtained sample provided relatively sharp peaks. Thus, the ion exchange of  $H^+$  for  $TMA^+$  probably occurred; however, we do not know to what extent the ion exchange progressed. Moreover, this ion exchange was also conducted at a molar ratio of  $TMA^+/H^+ = 2$  and 200. At  $TMA^+/H^+ = 2$ ,  $H_4Ta_6O_{17} \cdot nH_2O$

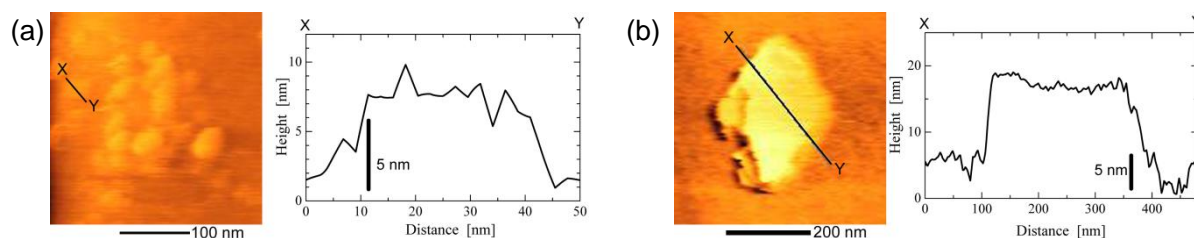
was present even after the ion exchange process. At  $\text{TMA}^+/\text{H}^+ = 200$ , the peak shift in XRD pattern occurred as well as at  $\text{TMA}^+/\text{H}^+ = 20$ . However, the XRD peaks became much broader by the ion exchange. Thus, a molar ratio around  $\text{TMA}^+/\text{H}^+ = 20$  was desirable, although the extent of ion exchange was unclear.

## (2) Synthesis procedure of $\text{MTaO}_3 \cdot n\text{H}_2\text{O}$ compounds

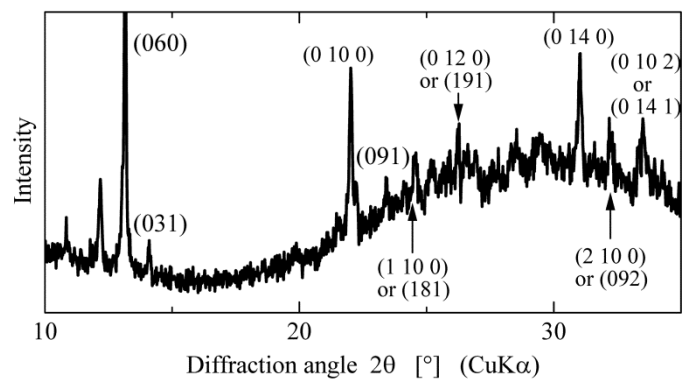
Also for monotantalates, three types of compounds were synthesized;  $\text{RbTaO}_3 \cdot n\text{H}_2\text{O}$ ,  $\text{HTaO}_3 \cdot n\text{H}_2\text{O}$ , and  $(\text{TMA},\text{H})\text{TaO}_3 \cdot n\text{H}_2\text{O}$ .  $\text{RbTaO}_3$  was synthesized by a solid state reaction, as follows:  $\text{Rb}_2\text{CO}_3$  powder (4.51 mmol) and  $\text{Ta}_2\text{O}_5$  powder (4.43 mmol) were mixed at a molar ratio of  $\text{Rb}/\text{Ta} = 1.02/1$ . The mixture was annealed at  $800\text{ }^\circ\text{C}$  for 2 h, and then ground by agate mortar and pestle. Further annealing at  $900\text{ }^\circ\text{C}$  for 20 h resulted in the formation of  $\text{RbTaO}_3$ .

$\text{HTaO}_3 \cdot n\text{H}_2\text{O}$  was prepared from  $\text{RbTaO}_3$  by ion exchange. The synthesized  $\text{RbTaO}_3$  (0.45 g) was added to 1 M HCl aqueous solution (45 mL). This mixing ratio corresponds to  $\text{H}^+/\text{Rb}^+ = 31.5$ . The resulting suspension was stirred at room temperature for 1 day. The powder was collected by centrifugation, and then washed with a copious amount of distilled water. This sequence of the ion exchange and washing processes was repeated four times. The powder obtained thus was allowed to dry under the ambient condition. Since the annealing of the powder at  $800\text{ }^\circ\text{C}$  provided  $\text{Ta}_2\text{O}_5$  powder, most  $\text{Rb}^+$  ions in the interlayers were likely ion-exchanged for  $\text{H}^+$ . Thus,  $\text{HTaO}_3 \cdot n\text{H}_2\text{O}$  was prepared.

$(\text{TMA},\text{H})\text{TaO}_3 \cdot n\text{H}_2\text{O}$  was prepared from  $\text{HTaO}_3 \cdot n\text{H}_2\text{O}$  by ion exchange. The synthesized  $\text{HTaO}_3 \cdot n\text{H}_2\text{O}$  (50 mg) was added to 15% TMAOH aqueous solution (26.4 mL). This mixing ratio corresponds to  $\text{TMA}^+/\text{H}^+ = 200$ . The resulting suspension was stirred at room temperature for 2 weeks. The powder was collected by centrifugation, washed with a copious amount of distilled water, and then allowed to dry under the ambient condition. This ion exchange shifted the peaks in the XRD patterns to lower angles; however, the XRD peaks became broader. The ion exchange of  $\text{H}^+$  for  $\text{TMA}^+$  probably occurred; however, we do not know to what extent the ion exchange progressed. This powder was used as  $(\text{TMA},\text{H})\text{TaO}_3 \cdot n\text{H}_2\text{O}$  sample.



**Figure S1** AFM images of the colloidal tantalate crystals and height profile along the line X-Y.



**Figure S2** The weak peaks in the XRD pattern of the sample prepared at  $R = 0.7$ .